[CONTRIBUTION FROM THE APPLIED SCIENCE RESEARCH LABORATORY OF THE UNIVERSITY OF CINCINNATI]

Chlorination of Natural and Synthetic Polyisoprenes

BY GERARD KRAUS[1] AND W. B. REYNOLDS

Introduction

Since natural rubber was first chlorinated in 1859,[2] a large amount of work has been directed toward elucidation of the mechanism of the chlorination.[3] While the early work in this field correctly established that the chlorination of rubber involves both substitution and addition, the recent classical work of Bloomfield[4] has provided a basic understanding of the various reactions involved.

In view of the considerable interest in synthetic polymers, it seemed of interest to study in detail the chlorination of synthetic polyisoprene and to compare that elastomer with Hevea (*cis*) natural polyisoprene and Gutta Percha (*trans*) natural polyisoprene. Synthetic polyisoprene contains both *cis* and *trans* internal double bonds and, in addition, differs from the natural polyisoprenes in that approximately 10 per cent. of the double bonds are in vinyl side chains resulting from 1–2 rather than 1–4 addition of monomer units during the polymerization. D'Ianni and co-workers[5] have reported a close similarity in the properties of chlorinated synthetic polyisoprene and chlorinated Hevea rubber.

Present Investigation

Using a refinement of the chlorination technique of Bloomfield[4] the substitutive and additive reactions of chlorine with emulsion polyisoprene, Hevea and Gutta Percha were followed quantitatively. Results are summarized graphically in Figs. 1–4 in which the curves numbered one represent the number of chlorine atoms per isoprene unit in the chlorinated polymers as a function of the number of Cl_2 molecules reacted per isoprene unit. Curves two and three represent the substitutive and additive chlorine atoms, respectively, also as a function of total Cl_2 molecules reacted per isoprene unit.

Figure 1 essentially confirms the results of Bloomfield[4] and additionally indicates that the *trans* Gutta Percha is quite similar to the *cis* Hevea. The chlorination proceeds in three stages, (a) the first molecule of chlorine reacting leads almost exclusively to substitution, (b) the next 1.2 molecules of chlorine react by both substitution and addition and (c) when approximately 2.2 molecules of chlorine per isoprene unit have reacted, the additive reaction ceases abruptly and all further reaction occurs by substitution. Under the mild conditions employed, reaction ceases when the chlorine content of the polymer is approximately 64 per cent. corresponding to about 3.38 atoms of chlorine per isoprene unit. Our results at 30° show that at this point a total of 2.81 moles of Cl_2 have reacted, 2.24 moles (80%) of which have reacted substitutively. This compares with 84% reacting substitutively in Bloomfield's experiments at 77° in daylight. The difference is due to the slightly different reaction conditions.

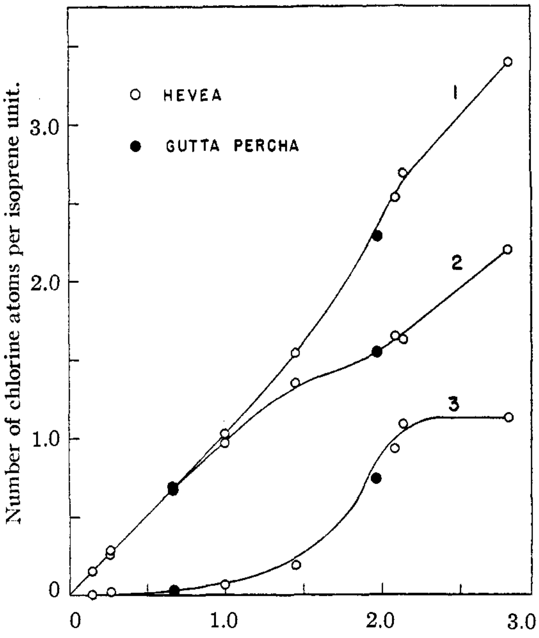

Fig. 1.—Addition and substitution in the chlorination of hevea and gutta percha at 30° and in the presence of an antioxidant: 1, total chlorine; 2, substitutive; 3, additive.

Figure 2 gives the results of the chlorination of synthetic polyisoprene in the dark and in the presence of an antioxidant. The similarity between these results and those obtained with the natural polyisoprenes is marked. However, the slight differences observed are significant in interpreting the results. The additive reaction for the synthetic polyisoprene ceases abruptly when

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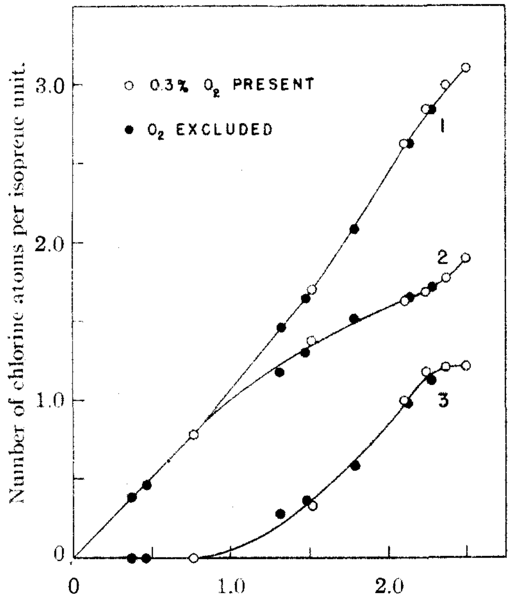
[1] This paper is based upon a thesis submitted by Gerard Kraus to the Graduate Faculty of the University of Cincinnati in partial fulfillment of the requirements for the degree of Doctor of Science.

[2] G. A. Engelhard and H. H. Day, British Patent 2734 (1859).

[3] (a) J. H. Gladstone and W. Hibbert, *J. Chem. Soc.*, **53**, 682 (1888); (b) J. McGavack, *Ind. Eng. Chem.*, **15**, 961 (1923); (c) F. Kirchhof, *Gummi Ztg.*, **46**, 497 (1932); (d) A. Nielsen, "Chlorkautschuk and die uebrigen Halogenverbindungen des Kautschuks," Verlag Hirzel, Leipzig, 1937, pp. 38–52; (e) C. H. Schweitzer, *Kautschuk*, **15**, 152 (1939); (f) J. Daubigny, *Rev. gen. Matieres plast.*, **14**, 17 (1938); (g) J. P. Baxter, *Chem. and Ind.*, **55**, 407 (1936); (h) H. Staudinger, *Ber.*, **57**, 152 (1924); *Kautschuk*, **17**, 101 (1941); (i) G. F. Bloomfield, E. H. Farmer and C. H. Miller, *J. Soc. Chem. Ind.*, **54**, 266T (1935).

[4] (a) G. F. Bloomfield, *J. Chem. Soc.*, 289 (1943); (b) 114 (1944).

[5] J. D. D'Ianni, F. J. Naples, J. W. Marsh and J. L. Zarney, *Ind. Eng. Chem.*, **38**, 1171 (1946).

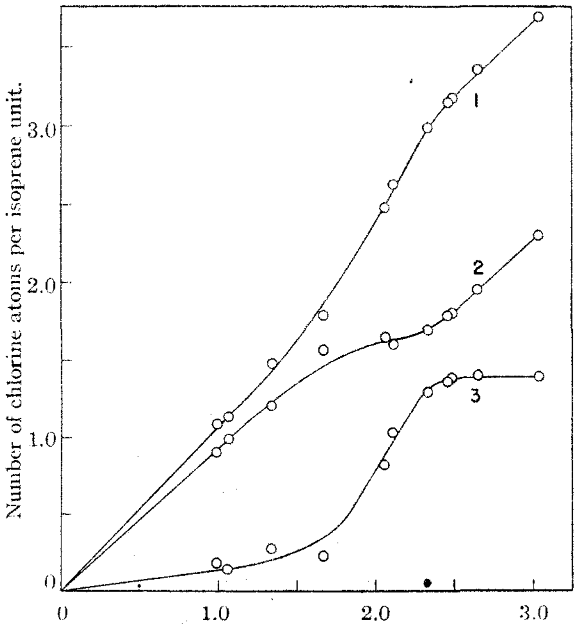


Moles of chlorine reacted with one base mole of polyisoprene.

Fig. 2.—Extent of additive and substitutive chlorination of emulsion polyisoprene in the dark: 1, total chlorine; 2, substitutive; 3, additive.

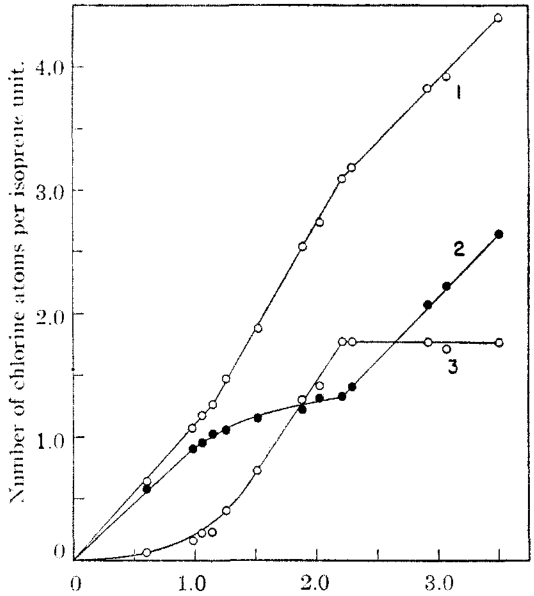
2.3 moles of chlorine have reacted. At this stage 75% of the chlorine has reacted substitutively.

Figure 3 gives the results of chlorination in diffuse daylight, in the absence of antioxidant and with approximately 0.3 volume per cent. of oxygen in the chlorine stream. A definite shift toward additive reaction can be observed. A very pronounced shift toward additive reaction was obtained when 1% benzoyl peroxide (based on polyisoprene) was added to the polyisoprene solution and the reaction vessel was irradiated during chlorination with a 100-watt mercury arc lamp (Fig. 4).



Moles of chlorine reacted with one base mole of polyisoprene.

Fig. 3.—Extent of addition and substitution in the chlorination of polyisoprene in the presence of small amounts of oxygen and light: 1, total chlorine; 2, substitutive; 3, additive.



Moles of chlorine reacted with one base mole of polyisoprene.

Fig. 4.—Extent of addition and substitution in the peroxide plus ultraviolet catalyzed chlorination of polyisoprene: 1, total chlorine; 2, substitutive; 3, additive.

The limit of additive reaction under the conditions of Fig. 2 is 1.21 chlorine atoms per isoprene unit. Straight addition to the double bond would require a value of two for this quantity. The lower value is due to cyclization as will be discussed more fully in a later section.

Figures 3 and 4 show that it is possible to favor the additive reaction at the expense of the cyclization by changing the reaction conditions. Additional experiments on the separate effects of benzoyl peroxide and light showed that peroxide alone does not favor addition, even though it strongly catalyzes the substitutive reaction. Ultraviolet light causes a strong shift toward addition. Only in the presence of both light and peroxide was it possible to carry the chlorination to the very high chlorine content indicated in Figure 4. (Final polymer contained 70.4 per cent. chlorine or 4.39 chlorine atoms per isoprene unit.)

Figure 5 shows the decrease in unsaturation of polyisoprene as a function of the per cent. chlorine in the product chlorinated under the conditions of Fig. 2. Values in the range 0 to 30% chlorine

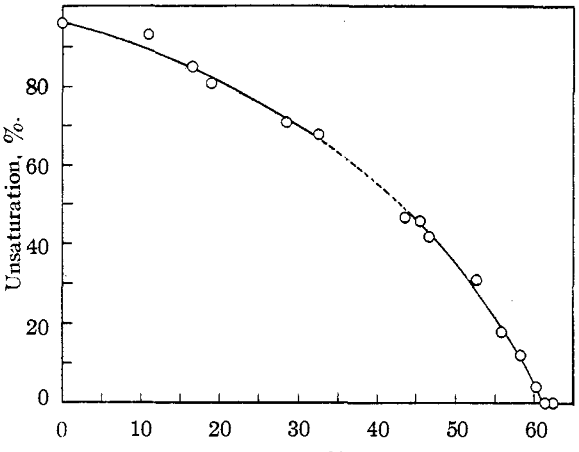


Fig. 5.—Unsaturation of chlorinated polyisoprenes.

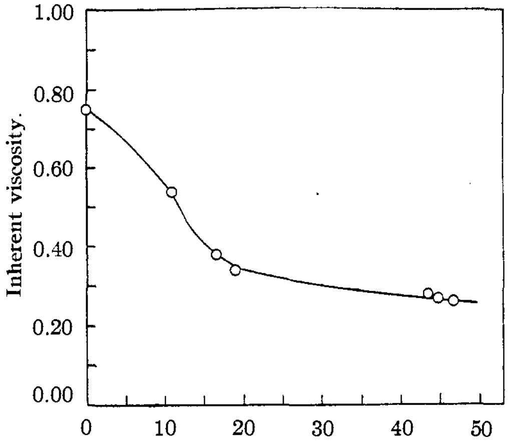
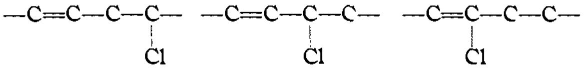


Fig. 6.—Inherent viscosity drop in early stages of chlorination of polyisoprene.

were obtained by iodine chloride titration according to the method of Kemp and Mueller.[6]

The applicability of the iodine chloride titration to chlorinated olefins and chlorinated rubber has been investigated by Bloomfield.[4b] Of the following groups



$$-C{=}C{-}C{-}\underset{\mathrm{Cl}}{C}- \qquad -C{=}C{-}\underset{\mathrm{Cl}}{C}{-}C- \qquad -C{=}\underset{\mathrm{Cl}}{C}{-}C{-}C-$$

only the last one inhibits iodine chloride addition to the double bond. Since in the case of chlorinated rubbers of low chlorine content (not more than one Cl atom per isoprene unit) practically all the substitutive chlorine is removable with alcoholic silver nitrate,[4b] the chlorine cannot be in the 2-position[7] and the iodine value should give a true measure of unsaturation.

Unsaturation in the 42–64% range was calculated from the remaining additive chlorine. This is a correct measure of unsaturation if the cyclization is complete below 40%.

Figure 6 shows the decrease in inherent viscosity of a sample of polyisoprene chlorinated under the conditions of Fig. 2. Since it has been shown by Staudinger and Staudinger[8] that no appreciable depolymerization takes place in the chlorination of rubber hydrocarbon in the absence of light and oxygen, the rapid decrease in the inherent viscosity during the early stages of the chlorination of synthetic polyisoprene may be ascribed to cyclization. While it is true that inherent viscosity changes of this order of magnitude might also be effected through a change in polymer–solvent interaction, it appears to the authors that in the case of chlorinated polyisoprene in carbon tetrachloride this change would be toward increased solvation and hence larger inherent viscosities. On the basis of these considerations the cyclization reaction appears to be essentially complete below 40% chlorine.

Discussion

Examination of Fig. 2 indicates that the total amount of chlorine which can be added to the double bonds is only somewhat more than half of the amount that could be expected to add on the basis of the initial unsaturation of the polyisoprene chlorinated. Since fully chlorinated polyisoprene contains no double bonds,[5] about half of the initial unsaturation is lost by cyclization. If the cyclization is visualized as involving the formation of six-membered rings, the possibility of a reaction by pairs is suggested. One of the principal features of this type of reaction is the isolation of reactive units between reacted pairs. The possibility of isolation of reactive units was first recognized by Flory, who developed a statistical treatment for calculating the number of such units.[9] Applying the statistics of reactions by pairs to the cyclization of polyisoprene or rubber, one obtains for the fraction of isoprene units incapable of undergoing cyclization

$$\frac{1}{n}\sum_{s=0}^{n-1}(-2)^s(n-s)/s! \qquad (1)$$

where n is the number of consecutive isoprene units in the chain. For chains of more than eight isoprene units, this reduces to

$$0.1353(1+2/n) \qquad (2)$$

to a close degree of approximation.

For long, uninterrupted chains of isoprene units, such as can be expected to occur in natural rubber the fraction of uncyclized units would be approximately 0.135. Hence, the theoretical limit of additive chlorine would be 1.135 atoms per isoprene unit. The value found (Fig. 1)

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[6] A. R. Kemp and G. S. Mueller, *Ind. Eng. Chem., Anal. Ed.*, **6**, 52 (1934).

[7] K. Ziegler, A. Spath, E. Schaaf, W. Schumann und E. Winkelmann, *Ann.*, **551**, 80 (1942).

[8] H. Staudinger and Hansjurgen Staudinger, *J. prakt. Chem.*, **162**, 148 (1943); *Rubber Chem. Tech.*, **17**, 15 (1944).

[9] P. J. Flory, THIS JOURNAL, **61**, 1518 (1939).

was 1.14. It is significant in this connection that the unsaturation of completely cyclized rubber (Thermoprene SL)[10] is 57% in excellent agreement with equation (1).

In the example of synthetic polyisoprene the problem is more complicated. Polyisoprene prepared by emulsion polymerization contains approximately 10% external double bonds due to 1-2 and/or 3-4 addition during polymerization. These cannot be expected to undergo cyclization in the same manner as the normal 1-4 isoprene units. Further, the total unsaturation of emulsion polyisoprene is slightly less than the theoretical. Assuming that these side chains and saturated units are lost to cyclization, it is still possible to estimate the total amount of additive chlorine. For polyisoprene of 96% unsaturation and containing 10% external double bonds we shall consider the spacing of the 1,2-addition units and the saturated units as entirely random. We shall further assume that only unsaturated 1,4-units are capable of undergoing cyclization. The statistical problem is then the same as in the removal of chlorine from copolymers of vinyl chloride, a case which has been treated by Wall.[11] The fraction of isolated units is given by Wall's calculation as e^{-2x}. In our example $x = 0.86$, so that the fraction of isoprene units isolated is 0.179. The total amount of chlorine necessary to saturate all cyclized units, isolated units and external double bonds is then readily calculated as 1.22 chlorine atoms per isoprene unit. The experimental value is 1.21 (Fig. 2).

The sharp inherent viscosity drop observed in the early stages of the polyisoprene chlorination (Fig. 6) suggests that cyclization precedes the additive reaction, a condition tacitly assumed in the statistical discussion. This is further borne out by the unsaturation of the low chlorine polymers as shown in Fig. 5. The amount of cyclization as calculated from unsaturation in the early stages of the chlorination is given in Table I.

TABLE I

CYCLIZATION IN THE EARLY STAGES OF CHLORINATION OF SYNTHETIC POLYISOPRENE AS DETERMINED BY IODINE CHLORIDE TITRATION

% Cl in polymer	% Unsat. by I–Cl	Cyclization, double bonds lost/ isoprene unit[a]	Substitutive Cl per isoprene unit	Ratio subst. Cl to cyclization
0.0	96	0.00	0.00	...
16.6	85	.11	.38	3.4
19.0	81	.15	.46	3.1
28.6	71	.27	.77	2.9
32.6	68	.29	.89	3.1

[a] Theoretical limit is 0.36.

The last column of Table I indicates that, during the early stages of chlorination, there are approximately three chlorine atoms substituted for each double bond lost through cyclization, *i. e.*, the cyclization reaction appears to be brought about by the third chlorine molecule reacting with a particular isoprene unit. Alternatively the cyclization may be induced by the first (or second) chlorine molecule reacting, followed by rapid substitution of two (or one) more chlorines in the cyclized unit.

One of the essential features of the statistical treatment of the cyclization reaction is that there can be no appreciable addition of chlorine to double bonds other than those occurring in already cyclized units (or vinyl side chains) until all the cyclization is complete. After this, the isolated units add chlorine. The data support this hypothesis. At 36.2% chlorine the degree of cyclization is 0.29 but additive chlorine is only 0.02 (probably resulting from addition to cyclized units). In the presence of light and peroxide the additive chlorine is much greater (Fig. 4). Under these conditions addition can apparently occur prior to cyclization thus increasing the number of isolated units and decreasing the ultimate degree of cyclization. Thus, the total ultimate additive chlorine would be higher at the expense of cyclization. This is in agreement with experiment as shown by Fig. 4.

Experimental

Method.—The apparatus is shown diagramatically in Fig. 7. A slow stream of chlorine (12–20 cc./min.) and nitrogen in approximately equal proportions was introduced just below the surface of an agitated, dilute (20 grams/l.) solution of the purified polymer in reagent grade carbon tetrachloride. The evolved gases were passed through the condenser (C) and up the column (B) packed with metallic antimony and glass wool. Any chlorine escaping from the solution was removed by the antimony while the hydrogen chloride passed through the column into a 2 *N* sodium hydroxide solution in the trap (A).

Special tests showed that separation of chlorine and hydrogen chloride by the above method was quantitative provided that the antimony was first saturated with anhydrous hydrogen chloride. Consequently, the antimony used was first treated with anhydrous HCl and then blown free of adsorbed hydrogen chloride by a stream of dry nitrogen. As a precaution the standard alkali in the trap was checked for hypochlorite and antimony (from hydrolysis of $SbCl_5$ vapors possibly carried into the trap) after each run. Both tests were consistently negative.

Commercial chlorine was used in all chlorinations. The gas was scrubbed with concentrated sulfuric acid (N) and liquefied in a Dry Ice trap (L). Half of the liquid chlorine was distilled off and trapped in alkali (P). The residue, substantially free of oxygen and hydrogen chloride, was allowed to distill into the reaction flask (G). The switch from trap (P) to reactor (G) was accomplished simply by turning the three-way stopcock (J). In experiments in which total exclusion of oxygen was not desired, the distillation of the chlorine was omitted.

The purpose of using nitrogen as a diluent was two-fold. Nitrogen provides a neutral atmosphere and keeps the solution in trap (A) from sucking back into the system upon absorption of HCl. At the same time, secondary addition of HCl to the rubber molecule is prevented by the flushing action of the nitrogen.[4] Oxygen was removed from the nitrogen by passing the latter through a dilute solution of chromous sulfate[12] (U). The gas was then

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(10) Davis and Blake, "Chemistry and Technology of Rubber," Reinhold Publishing Corp., New York, N. Y., 1937, p. 659.

(11) F. T. Wall, THIS JOURNAL, 62, 803 (1940).

(12) F. F. Rust and W. E. Vaughan, *J. Org. Chem.*, 5 449 (1940)

scrubbed with concentrated sulfuric acid (T) and passed through a phosphorus pentoxide drying tube (S) before being mixed with the chlorine. Again, in experiments not necessitating the strict absence of oxygen, the procedure was simplified by omitting the chromous sulfate bubbler. The nitrogen used contained 0.3% oxygen by volume.

Before starting each chlorination, the entire system was blown out with nitrogen for at least 10 hours. Likewise, the nitrogen flow was continued after chlorination until the exit gases tested entirely neutral toward moist litmus paper. Total darkness during chlorination was insured by placing the entire apparatus in a blacked out laboratory hood.

Chlorinations under ultraviolet light were run with the reactor flask irradiated by a 100 watt mercury arc light source.

Phenyl-β-naphthylamine was used whenever chlorination was carried out in the presence of an antioxidant. Its purification was accomplished by recrystallizing technical phenyl-β-naphthylamine (Eastman Kodak Co.) twice from alcohol. The preparation of the samples and the analytical procedures used are given in the following paragraphs.

Preparation and Purification of Polymers for Chlorination

Polyisoprene.—Since a reproducible source of polyisoprene was required, polyisoprene was prepared in the laboratory from isoprene supplied by Newport Industries. The isoprene was distilled to remove the polymerization inhibitor and polymerized in the following emulsion recipe:

Isoprene	100.0 g.
Phillips tertiary hexadecyl mercaptan	0.5 g.
Water	180.0 g.
Potassium persulfate	0.3 g.
Soap (Procter and Gamble SF flakes)	5.0 g.

The polymerizations were carried out in 12 oz. crown-capped bottles, rotated end over end in a thermostat at 50° for 30 hours. The latex thus obtained was short-stopped with 0.06 g. of hydroquinone and stripped of unreacted monomer by vigorous stirring at 50–60°. Phenyl-β-naphthylamine (1.2 g.) was added as antioxidant. Coagulation of the latex was effected by addition of 100 cc. of ethanol. The resulting rubber was carefully washed free of soap in warm water and dried for 24 hours in a vacuum oven at 50°. This was followed by a 24 hour extraction (in a Soxhlet apparatus) with the azeotropic mixture of ethanol and toluene. In the extraction all but traces of antioxidant originally added to protect the polymer during the stripping and washing operations was removed along with residual monomer, low molecular weight polymer and soap. The rubber was again dried, this time for 48 hours at 35° *in vacuo*. The resulting polyisoprene hydrocarbon was a colorless, transparent, soft polymer of nearly theoretical iodine value. It was stored in the dark in an evacuated desiccator.

Hevea.—Pale crepe was purified by a method similar to that described by Kemp and Peters.[13] Fifty grams of crepe was placed in a cloth bag and submerged in 1500 cc. of chloroform to which 0.2 g. of phenyl-β-naphthylamine had been added. Diffusion of the rubber into the solvent was allowed to take place for five days, after which the rubber was precipitated with methanol and redissolved in benzene. The benzene solution was then fractionally precipitated with a 50-50 mixture of ethanol and benzene and the first fraction discarded. According to Pummerer and Koch[14] all impurities are removed with the first fraction. The rubber hydrocarbon was dried for 48 hours at 35° in a vacuum. Iodine chloride titration gave an iodine value of 370 for the final product (99% of theoretical).

Gutta Percha.—Crude gutta percha was dissolved in benzene and the solution filtered to remove grit and sand. The polymer was then precipitated with alcohol and extracted with the azeotropic mixture of ethanol and toluene. After two more precipitations, the product was dried in the manner described for polyisoprene and Hevea. The purified material had an iodine value of 364 (97% of theoretical).

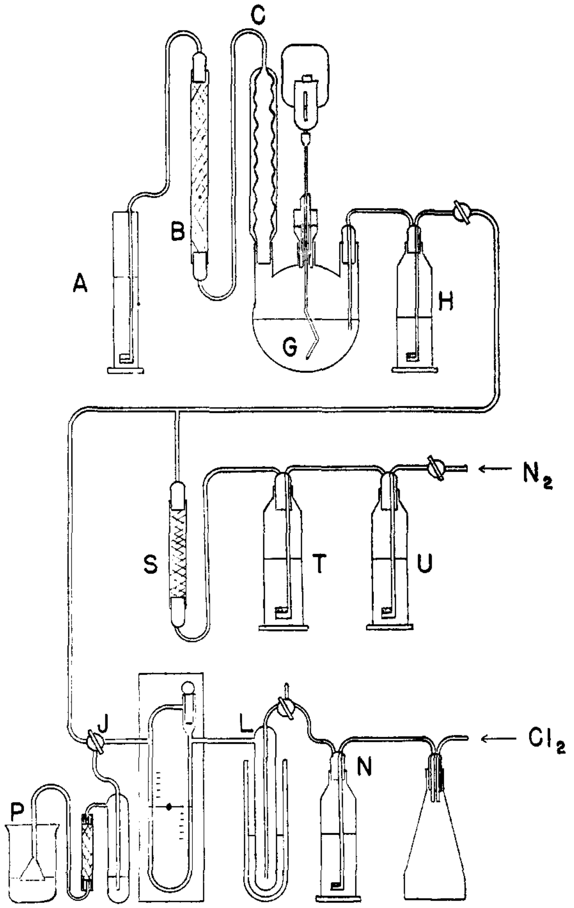

Fig. 7.—Apparatus for controlled chlorination of polymers.

Isolation of Chlorination Products.—The chlorinated polymers were isolated from the CCl_4 solution by dropping the solution into boiling water to flash off the solvent. The product was then divided up into small pieces and washed in boiling tap water for 30 minutes. This was followed by a similar wash in distilled water. The polymer was carefully dried in a vacuum oven at 50°.

The drastic treatment to remove the solvent is absolutely essential, since chlorinated rubbers are particularly apt to retain traces of solvents.[15] It was realized that boiling of the polymers might cause hydrogen chloride to be split off. However, in all but a few cases, no chloride could be detected in the wash water. Even when the water gave a positive test for chloride, the amount was quite negligible.

It was found convenient to precipitate polymers of low chlorine content with ethanol prior to boiling them in water. This was done merely to facilitate handling of the inherently sticky polymers.

Analytical Methods

Chlorine Analyses.—The pure, dry polymers were analyzed for chlorine by sodium peroxide fusion (Parr bomb technique) followed by Volhard titration.

The amount of hydrogen chloride evolved during the chlorination was determined by titration of an aliquot from the standard alkali. The Volhard chloride determination was favored over back-titration with standard acid as a

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(13) A. R. Kemp and H. Peters, *Ind. Eng. Chem.*, **33**, 1391 (1941).

(14) R. Pummerer and A. Koch, *Ann.*, **438**, 294 (1924).

(15) R. Houwink, "Chemie und Technologie der Kunststoffe," Akademische Verlagsgesellschaft m. b. H., Leipzig, 1939, p. 481.

matter of convenience. No difficulty was encountered from traces of carbon tetrachloride swept into the alkali trap during chlorination.

Iodine Chloride Titrations.—The limitations of the iodine chloride titration have been discussed. The method of Kemp and Mueller[16] was applied successfully without modifications to polyisoprene, rubber and gutta percha. However, with chlorinated polymers the procedure had to be modified to insure complete iodine chloride addition. The reason for this is two-fold: (1) the reaction is considerably slower for the chlorinated polymers, and (2) the low solubility of some of the chlorinated polymers further retards iodine chloride addition and leads to erratic results, as the titration must be carried out with a gel containing sample. These difficulties were largely overcome by allowing additional time for the iodine chloride addition to take place.

Summary

The extent of additive and substitutive chlorination was determined for emulsion polyisoprene, Hevea and Gutta Percha chlorinated to different chlorine contents in the dark and in a nitrogen atmosphere.

The maximum amount of additive chlorine that can be introduced into the polymer is 1.21 atoms of chlorine per isoprene unit for synthetic emulsion polyisoprene, 1.14 for Hevea. The chlorination involves a cyclization reaction by pairs, leading to isolation of reactive units. The loss in unsaturation due to cyclization has been calculated statistically by the method of Flory and Wall and has been shown to be consistent with the total amount of additive chlorine in the fully chlorinated product.

The cyclization takes place in the early stages of the chlorination simultaneously with the initial substitution. The theoretical limit of cyclization calculated statistically is 86.5% of all isoprene units cyclized for natural rubber and 72% for polyisoprene containing 10% vinyl side chains.

Iodine chloride titration gives fair results for samples of low chlorine content but is not applicable to polymers containing much more than 35% Cl. Knowing the degree of cyclization, the unsaturation can, however, be calculated for any polymer from the extent of additive reaction.

Substitutive chlorination is catalyzed by oxygen and peroxide, additive chlorination by ultraviolet light. Cyclization is partially prevented by the increase in additive reaction. Under the combined effect of peroxides and ultraviolet radiation chlorination can be carried to very high degrees.

BARTLESVILLE, OKLAHOMA RECEIVED APRIL 21, 1949

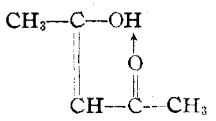
[16] A. R. Kemp and G. S. Mueller, *Ind. Eng. Chem., Anal. Ed.*, **6**, 52 (1934).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Determination of Bond Fixation in Cyclic Systems. I. Naphthalene

BY I. MOYER HUNSBERGER[1]

A comparison of the infrared spectra of the enolic form of acetylacetone (I) (containing OH conjugated with C=O) with the corresponding saturated compound (II) (containing OH not conjugated with C=O) has demonstrated the absence of chelation in the latter.[2]



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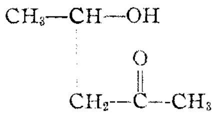

II

Although in some cases chelation apparently is possible without conjugation between the chelated groups, there seems no doubt that the most strongly chelated compounds owe their character to a high degree of conjugation. These "conjugated chelate" systems recently have been adequately discussed.[3]

If chelated substituents are present on an aromatic ring, the strength of chelation obviously should depend on the degree of "doublebondedness" of the bond joining the ring carbon atoms holding the substituents. Thus, Calvin and Melchior[4] recently found that metallic chelates derived from 3-hydroxy-2-naphthaldehyde were less stable than those from its 1,2- or 2,1- isomers. They attributed this behavior to the greater double bond character of the nuclear C_1–C_2 bond as compared to the C_2–C_3 bond. Melchior[5] also has explained differences in the ultraviolet spectra of these aldehydes on the same basis. Baker[6] earlier had pointed out that any difference in the strength of chelation between isomeric 1,2- (or 2,1-) and 2,3- disubstituted naphthalenes could be explained on the basis of a more or less fixed nuclear double bond structure. However, from a comparison of the wet melting points and critical solution temperatures of the 1,2-, 2,1- and 3,2- hydroxyacetonaphthones Baker[6] concluded that all isomers apparently were almost equally strongly chelated. As a result, an obviously attractive physical method for detecting bond fixation by measuring the strength of chelation in appropriate *o*- disubstituted isomers of a given ring system failed to materialize.

Other physical methods which have been used

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[1] Department of Chemistry, Antioch College, Yellow Springs, Ohio.

[2] Freymann and Heilmann, *Compt. rend.*, **219**, 415 (1944).

[3] (a) Rasmussen, Tunnicliff and Brattain, THIS JOURNAL, **71**, 1068 (1949); (b) Rasmussen and Brattain, *ibid.*, **71**, 1073 (1949).

[4] Calvin and Melchior, *ibid.*, **70**, 3273 (1948).

[5] Melchior, *ibid.*, **71**, 3647 (1949).

[6] Baker and Carruthers, *J. Chem. Soc.*, 479 (1937).